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Structured liquid detergents with selected perfume fragrance materials

(57) Heavy duty gel or liquid laundry detergent compositions comprise, an anionic surfactant, a perfume composition and a structurant; the perfume composition includes specially selected hydrophobic fragrance materials which can be incorporated into a lamellar phase in the detergent composition thus suppressing the overall odor intensity of the detergent composition. Other components of the composition include citric acid, enzymes, brighteners, ethanol, monoethanolamine, caustic soda, borax, suds suppressor and a dye.

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STRUCTURED LIQUID DETERGENTS WITH SELECTED PERFUME FRAGRANCE MATERIALS

FIELD OF THE INVENTION

This invention relates to structured liquid or gel laundry detergent products comprising an anionic surfactant, a structurant and specially selected hydrophobic, low volatility perfumes.

BACKGROUND OF THE INVENTION

Liquid laundry detergent products offer a number of advantages over dry, powdered or particulate laundry detergent products. Liquid laundry detergent products are readily measurable, speedily dissolved in wash water, non-dusting, are capable of being easily applied in concentrated solutions or dispersions to soiled areas on garments to be laundered and usually occupy less storage space than granular products. Additionally, liquid laundry detergents may have incorporated into their formulations materials which would deteriorate in the drying operations employed in the manufacture of particulate or granular laundry detergent products. Because liquid laundry detergents are usually considered to be more convenient to use than granular laundry detergents, they have found substantial favor with consumers.

However, the formulation of liquid laundry detergent compositions also presents difficulties, particularly in regard to incorporating perfumes into the detergent compositions. Perfumes are formulations of one or more constituent fragrance materials. A formulator of perfume compositions selects these fragrance materials so that the overall perfume composition has a scent that conveys freshness and cleanliness to a consumer when the scent is deposited on a garment or other textile article. Because the most immediate perception that a consumer has of the effectiveness of a laundry detergent composition is the scent that the detergent composition has imparted to textile articles, it is extremely important that the detergent composition deliver sufficient, enduring perfume composition to the surface of textile articles to provide a perceptible signal to a consumer that the detergent compositions have provided substantial cleaning and refreshing benefits. It is equally important that when this perfume is delivered to the surface of a textile article, it is retained through both subsequent washing and drying processes.

There are at least two reasons why perfumes included in a detergent composition may nonetheless not provide freshening benefits to a textile article after successive washing and drying processes. First, during an aqueous wash process (such as in a domestic clothes washer) the perfumes may be absorbed into the aqueous laundry detergent solution rather than being imparted to the surface of the textile article. A second reason is that perfumes may be degraded

and evaporated in a heated environment, such as a domestic clothes dryer. Thus it is often necessary to incorporate relatively high levels of perfume into a detergent composition in order to insure that a satisfactory amount of perfume is delivered to the surface of the textile article and then retained on the surface through subsequent washing and drying processes. But these high levels of perfume in a detergent composition can be difficult to stabilize and may give the liquid detergent composition a pungent, strong odor that many consumers dislike.

One alternative to using high, malodor-causing levels of perfume composition is to include in the perfume composition certain hydrophobic fragrance materials which are especially likely to be retained on the surface of a garment or textile article during washing and drying. Because these fragrance materials are hydrophobic, they are more likely to cling to a hydrophobic surface like the surface of a textile article, and less likely to be absorbed into the aqueous laundry detergent solution. However, even when included at lower concentrations, hydrophobic materials may still contribute to the pungent, strong odor to which most consumers are adverse.

Thus there is a continuing need for laundry detergent compositions which can deliver to the surface of a textile article perfumes which are likely to be retained through both subsequent washing and drying of the textile article. Accordingly a benefit of the present invention is that a liquid laundry detergent composition is provided which contains a perfume component that imparts a pleasing and enduring scent to textile and garment articles during a washing process but the detergent composition lacks the strong, pungent perfume odor that is undesirable to consumers.

Nearly all liquid detergent compositions can be classified as being either "structured" or isotropic liquids. Isotropic liquids are homogeneous, all of the ingredients having been dissolved into the solvent. By contrast, in an internally structured liquid, while some of the ingredients may have been dissolved in the solvent, there are also ordered liquid crystal structures. Without being limited by theory, it is believed that the shape of the liquid crystal is determined by the preferred geometric packing arrangement. In the case of amphiphiles such as ionic surfactants, the packing arrangement is strongly influenced by the size of the hydrophilic polar head group and the strength in the liquid mixture of electrostatic forces which attract or repel the polar head group. In addition to providing a pleasing fragrant scent hydrophobic fragrance materials also offer another important benefit: because of their hydrophobicity it is possible incorporate the fragrance materials into an internally structured liquid detergent, thereby lowering the overall odor intensity that the perfume contributes to the detergent composition.

Thus without intending to be limited by theory, it is believed that fragrance materials can be incorporated into the highly hydrophobic areas of the lamellar liquid crystals which are contained in the structured liquid detergent composition thereby suppressing the odor intensity of the fragrance materials and thus reducing the odor intensity of the detergent composition. When the detergent composition is then dissolved in water to form a detersive aqueous solution, the lamellar phase melts and the fragrance materials are released into the aqueous solution where they are subsequently deposited on the surface of a textile article.

SUMMARY OF THE INVENTION

It has now been determined that when certain hydrophobic fragrance materials are incorporated into a structured liquid laundry detergent composition, such detergent compositions will impart a durable scent to the textile articles washed in the detergent compositions without giving the detergent compositions themselves an unpleasant odor which is adverse to consumers. It is thus a benefit of the present invention that an internally structured liquid or gel laundry detergent composition is provided which has excellent cleaning performance, acceptable product rheology and imparts a pleasing and enduring scent to a textile article.

In a first aspect, the present invention encompasses a heavy duty liquid or gel laundry detergent compositions comprising, by weight of the composition:

a) from about 10% to about 40% of an anionic surfactant;

b) a perfume composition, wherein at least about 1% of the perfume composition comprises fragrance materials selected from the group consisting of fragrance materials having a logP of at least about 3.

c) a structurant.

In a second aspect, the present invention encompasses a heavy duty liquid or gel laundry detergent compositions which is either wholly or partly in lamellar form and comprises

a) from about 10% to about 40% of an anionic surfactant;

b) from about 0.1 % to about 3.0% of a perfume composition, wherein at least about 1 % of the perfume composition comprises fragrance materials selected from the group consisting of fragrance materials having a logP of at least about 3.

c) at least 0.5 % of a structurant;

d) an amine selected from the group consisting of detersive amines, modified polyamines, polyamide-polyamines, polyethoxylated-polyamine polymers, quaternary ammonium surfactants, and mixtures thereof;

wherein the viscosity of the detergent composition is from about 100 cps to about 4,000 cps when measured at a temperature of 25°C and at a shear rate of 20 s^{-1}.

All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified. All temperatures are in degrees Celsius (° C) unless otherwise specified. All documents cited are, in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

As used herein, "logP" includes logP values determined by observation or experimentation and those values obtained through calculation by the use of the CLOGP program.

By "transparent" it is meant that light is easily transmitted through the gel detergent compositions of the present invention and that objects on one side of the gel composition are at least partially visible from the other side of the composition.

The present invention includes a perfume composition selected to provide a fresh sensory impression on the surface of a textile article to which the perfume composition is imparted. The perfume composition is typically present at a level of from about 0.05 % to about 3.0 %, preferably from about 0.1 % to about 2 %, most preferably from about 0.2 % to about 1 %, by weight of the detergent composition.

The perfume compositions are themselves comprised of fragrance material. It is an essential part of the present invention that some of these fragrance materials be hydrophobic. The degree of hydrophobicity of a fragrance material can be correlated with its octanol/water partitioning coefficient ("P"). The octanol/water partition coefficient of a fragrance material is the ratio between its equilibrium concentration in octanol and in water. A fragrance material with a greater partition coefficient P is more hydrophobic. Conversely, a fragrance material with a smaller partition coefficient P is more hydrophilic. In the present invention, hydrophobic fragrance materials are those with an octanol/water partition coefficient P of 1000 or greater. Since the partition coefficient of the fragrance materials normally have high value, they are more conveniently given in the form of their logarithm to the base 10, log P. Preferably, at least about 1 %, more preferably at least about 3 %, most preferably at least about 5 %, by weight, of the perfume composition is composed of fragrance materials which have logP values of at least 3. The composition will also preferably contain no more than about 95 %, more preferably no more than about 90 %, most preferably no more than about 80 % of fragrance materials which have logP values of at least 3.

The logP of many perfume ingredients has been reported; for example, the Pomona92 database, available from Daylight Chemical Information Systems, Inc. (Daylog CIS), Irvine, Calif., contains many, along with citations to the original literature. However, the logP values are most conveniently calculated by the "CLOGP" program, also available from Daylight CIS. This program also lists experimental logP values when they are available in the Pomona92 database. The "calculated logP" (ClogP) is determined by the fragment approach of Hansch and Leo (cf., A. Leo, in Comprehensive Medicinal Chemistry, Vol. 4, C. Hansch, P. G. Sammens, J. B. Taylor and C. A. Ramsden, Eds., p. 295, Pergamon Press, 1990, incorporated herein by reference). The fragment approach is based on the chemical structure of each perfume ingredient, and takes into account the numbers and types of atoms, the atom connectivity, and chemical bonding. The ClogP values, which are the most reliable and widely used estimates for this physicochemical property, are used instead of the experimental logP values in the selection of perfume ingredients which are useful in the present invention.

Nonlimiting examples of suitable fragrance materials and their respective ClogP values include the following:

Fragrance Material	ClogP
Alpha-Hexylcinnamaldehyde	4.9
Alpha-Methylionone	4.5
Ambretone	6.0
Cetalox	5.0
Cis-3-Hexenyl Salicylate	4.6
Citronellal	3.3
Cyclamen Aldehyde	3.5
Cyclohexyl Salicylate	4.5
Dihydro Linalool	3.0
Dihydromyrcenol	3.0
Dimethyl Benzyl Carbinyl Acetate	3.1
Gamma-Dodecalactone	4.0
Gamma-Undecalactone	3.4
Geranyl Nitrile	3.3
Isobornyl Acetate	3.5
Lilial	4.1

N-Hexyl Salicylate	5.1
Nerol	3.1
Norlimbanol	5.9
Pentadecanolide	5.7
Phenethyl Phenylacetate	4.0
Polysantol	5.0
Rhodinol	3.3
Terpineol (Alpha,Beta,Gamma)	3.1
Tetrahydrolinalool	3.5
Tonalid	6.3
Trifone	4.0

To further increase the durability of the scents deposited on textile and garment articles, it may also be desirable to include fragrance materials in the perfume composition which are not only hydrophobic but are also of a low-volatility, meaning that they have a boiling point of at least 250°C. Because of their higher boiling points, these fragrance materials are less likely to be evaporated in a clothes dryer. If it is desired to use a fragrance material that is not only hydrophobic but of low-volatility then preferably, at least about 1 % , more preferably at least about 3 % , most preferably at least about 5 %, by weight, of the perfume composition is composed of fragrance materials which have logP values of at least 3 and boiling points of 250°C or greater. The composition will also preferably contain no more than about 90 %, more preferably no more than about 65 %, most preferably no more than about 55 % of fragrance materials which have logP values of at least 3 and boiling points of 250°C or greater.

Nonlimiting examples of suitable fragrance materials and their respective boiling points include the following:

Fragrance Material	Boiling Point (°C)
Alpha-Methylionone	281
Ambretone	338
Cetalox	280
Cis-3-Hexenyl Salicylate	316
Cyclamen Aldehyde	274
Cyclohexyl Salicylate	325
Gamma-Dodecalactone	288

Gamma-Undecalactone	260
Lilial	287
N-Hexyl Salicylate	311
Norlimbanol	297
Pentadecanolide	329
Phenethyl Phenylacetate	350
Polysantol	297
Tonalid	344
Trifone	444

Structurants - The detergent compositions herein contain at least 0.5 %, preferably at least 1.0%, more preferably at least 2.0% of a structurant. The selection and concentration of structurants is important because the particular combination of structurants and surfactants will determine whether the liquid detergent composition will be a structured liquid or an isotropic liquid.

Additionally, the combination and concentration of surfactants and structurants will also determine the viscosity of the detergent The rheology behavior can be modeled by the following formula:

$$\eta = \eta_0 + K\gamma^{(n-1)}$$

where η is the viscosity of the liquid at a given shear rate, η_0 is the viscosity at infinite shear rate, γ is the shear rate, n is the shear rate index, and K is the consistency. Structured liquid detergents are known to have an infinite shear viscosity (ηo) value between 0 and about 3,000cp (centipoise), a shear index (n) value of less than about 0.6, a consistency value, K, of above about 1,000, and a viscosity (η) measured at 20^{-1} of less than about 10,000cp, preferably less than about 5,000cp. Under low stress levels, a "zero shear" viscosity is above about 100,000cp wherein "zero shear" is meant a shear rate of 0.001 s^{-1} or less. The yield value of the compositions herein, obtained by plotting viscosity versus stress, is larger than 0.2Pa. These rheology parameters can be measured with any commercially available rheometer, such as the Carrimed CSL 100 model. The particular compositions of the present invention have a viscosity at 20 s^{-1} shear rate of from about 100 cps to about 4,000 cps, preferably from about 300 cps to about 3,000 cps, more preferably from about 500 cps to about 2,000 cps and are stable upon storage.

Materials which can perform the role of a structurant include electrolytes and builders. When included herein, these materials function not only as structurants but also perform in their conventional roles in a detergent composition.

Suitable for use herein are those electrolytes known as "salting-out" electrolytes. These include water-soluble builder salts, such as the alkali metal ortho- and pyrophosphates, the alkali metal tripolyphosphates, the alkali metal silicates, borates, carbonates, sulfates, alkali metal citrates, alkali metal salts of nitrilotriacetate, alkali metal salts of carboxymethyloxy succinate. Ammonium salts of the above anions may be used instead of alkali salts.

Detergent builders can optionally but preferably be included in the compositions herein, for example to assist in controlling mineral, especially Ca and/or Mg, hardness in wash water or to assist in the removal of particulate soils from surfaces, as well as to provide benefits as an electrolyte. Builder level can vary widely depending upon end use and physical form of the composition. Built detergents typically comprise at least about 1% builder. Liquid formulations typically comprise about 5% to about 50%, more typically 5% to 35% of builder. Lower or higher levels of builders are not excluded. For example, certain detergent additive or high-surfactant formulations can be unbuilt. Because they also function well as electrolytes, citrates are the most preferred.

Suitable builders herein can be selected from the group consisting of phosphates and polyphosphates, especially the sodium salts; silicates including water-soluble and hydrous solid types and including those having chain-, layer-, or three-dimensional- structure as well as amorphous-solid or non-structured-liquid types; carbonates, bicarbonates, sesquicarbonates and carbonate minerals other than sodium carbonate or sesquicarbonate; aluminosilicates; organic mono-, di-, tri-, and tetracarboxylates especially water-soluble nonsurfactant carboxylates in acid, sodium, potassium or alkanolammonium salt form, as well as oligomeric or water-soluble low molecular weight polymer carboxylates including aliphatic and aromatic types; and phytic acid.

Builder mixtures, sometimes termed "builder systems" can be used and typically comprise two or more conventional builders, optionally complemented by chelants, pH-buffers or fillers, though these latter materials are generally accounted for separately when describing quantities of materials herein.

Phosphorus containing detergent builders often preferred where permitted by legislation include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of

polyphosphates exemplified by the tripolyphosphates, pyrophosphates, glassy polymeric meta-phosphates; and phosphonates.

Suitable silicate builders include alkali metal silicates, particularly those liquids and solids having a SiO_2:Na_2O ratio in the range 1.6:1 to 3.2:1, including, particularly for automatic dishwashing purposes, solid hydrous 2-ratio silicates marketed by PQ Corp. under the trade name BRITESIL®, e.g., BRITESIL H2O; and layered silicates, e.g., those described in U.S. 4,664,839, May 12, 1987, H. P. Rieck. See preparative methods in German DE-A-3,417,649 and DE-A-3,742,043.

Also suitable for use herein are synthesized crystalline ion exchange materials or hydrates thereof as taught in U.S. 5,427,711, Sakaguchi et al, June 27, 1995.

Suitable carbonate builders include alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are especially useful in granular detergents, but can also be incorporated in liquids. Suitable for the present purposes are those having empirical formula: $[M_z(AlO_2)_z(SiO_2)_v]\cdot xH_2O$ wherein z and v are integers of at least 6, the molar ratio of z to v is in the range from 1.0 to 0.5, and x is an integer from 15 to 264. Aluminosilicates can be crystalline or amorphous, naturally-occurring or synthetically derived. An aluminosilicate production method is in U.S. 3,985,669, Krummel, et al, October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials are available as Zeolite A, Zeolite P (B), Zeolite X and, to whatever extent this differs from Zeolite P, the so-called Zeolite MAP.

Suitable organic detergent builders include polycarboxylate compounds, including water-soluble nonsurfactant dicarboxylates and tricarboxylates. More typically builder polycarboxylates have a plurality of carboxylate groups, preferably at least 3 carboxylates. Carboxylate builders can be formulated in acid, partially neutral, neutral or overbased form. When in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred. Polycarboxylate builders include the ether polycarboxylates, such as oxydisuccinate, see Berg, U.S. 3,128,287, April 7, 1964, and Lamberti et al, U.S. 3,635,830, January 18, 1972; "TMS/TDS" builders of U.S. 4,663,071, Bush et al, May 5, 1987; and other ether carboxylates including cyclic and alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other suitable builders are the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether; 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid; carboxymethyloxysuccinic acid; the various alkali metal, ammonium and substituted

ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid; as well as mellitic acid, succinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Oxydisuccinates are also especially useful in such compositions and combinations.

Certain detersive surfactants or their short-chain homologs also have a builder action. For unambiguous formula accounting purposes, when they have surfactant capability, these materials are summed up as detersive surfactants. Preferred types for builder functionality are illustrated by: 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. 4,566,984, Bush, January 28, 1986. Succinic acid builders include the C_5-C_{20} alkyl and alkenyl succinic acids and salts thereof. Succinate builders also include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Lauryl-succinates are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986. Fatty acids, e.g., C_{12}-C_{18} monocarboxylic acids, can also be incorporated into the compositions as surfactant/builder materials alone or in combination with the aforementioned builders, especially citrate and/or the succinate builders, to provide additional builder activity. Other suitable polycarboxylates are disclosed in U.S. 4,144,226, Crutchfield et al, March 13, 1979 and in U.S. 3,308,067, Diehl, March 7, 1967. See also Diehl, U.S. 3,723,322.

c) Solvents

By "solvent" is meant the commonly used solvents in the detergent industry, including alkyl monoalcohol, di-, and tri-alcohols, ethylene glycol, propylene glycol, propanediol, ethanediol, glycerine, etc.

d) Hydrotropes

By "hydrotrope" is meant the commonly used hydrotropes in the detergent industry, including short chain surfactants that help solubilize other surfactants such as aromatic sulphonates. Other examples of hydrotropes include cumene, xylene, or toluene sulfonate, urea, C_8 or shorter chain alkyl carboxylates, and C_8 or shorter chain alkyl sulfate and ethoxylated sulfates.

The compositions herein may optionally contain from about 0% to about 10%, by weight, of solvents and hydrotropes.

e) Aminocarboxylate Chelating Agents

The present detergent compositions may contain aminocarboxylate sequestrants, which without intending to be bound by theory, are believed to provide benefits to detergent

compositions because their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates. They can also function as structurants. Aminocarboxylates suitable for use in the present invention comprise one of the following amines:

$$—N—CH_2(CH_2COOH)(COOM), \text{ and}$$

$$—N(MOOCCH_2)_2,$$

M is selected from the group consisting of hydrogen, an alkali metal, ammonium and mixtures thereof. Suitable aminocarboxylate sequestrants include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetraproprionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

f) Other Chelating Agents Besides aminocarboxylates, the present detergent compositions may also include other chelating agents such as Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at lease low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. It is preferred that these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms. A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

Modified polyamine - The compositions herein may comprise at least about 0.05%, preferably from about 0.05% to about 3%, by weight, of a water-soluble or dispersible, modified polyamine agent, said agent comprising a polyamine backbone corresponding to the formula:

$$[(R^2)_2\text{-}N]_w\text{-}[R^1\text{-}N]_x\text{-}[R^1\text{-}N]_y\text{-}[R^1\text{-}N]_z$$
$$\qquad\qquad\quad |\qquad\qquad |\qquad\qquad |$$
$$\qquad\qquad\quad B\qquad\qquad R^2\qquad\qquad (R^2)_2$$

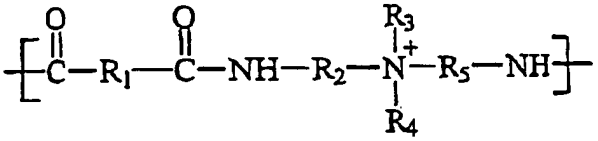
wherein each R^1 is independently C_2-C_5 alkylene, alkenylene or arylene; each R^2 is independently H, or a moiety of formula $OH[(CH_2)_xO]_n$, wherein x is from about 1 to about 8 and n is from about 10 to about 50; w is 0 or 1; x+y+z is from about 5 to about 30; and B represents a continuation of this structure by branching; and wherein said polyamine before alkylation has an average molecular weight of from about 300 to about 1,200.

In preferred embodiments, R^1 is C_2-C_4 alkylene, more preferably ethylene; R^2 is $OH[CH_2CH_2O]_n$, wherein n is from about 15 to about 30, more preferably n is about 20. The average Molecular Weight of the polyamine before alkylation is from about 300 to about 1200,

more preferably from about 500 to about 900, still more preferably from about 600 to about 700, even more preferably from about 600 to about 650.

Polyamide-Polyamines - The gel compositions of the present invention preferably comprise from about 0.1% to 8% by the weight of the composition of certain polyamide-polyamines. More preferably, such polyamide-polyamine materials will comprise from about 0.5% to 4% by weight of the compositions herein. Most preferably, these polyamide-polyamines will comprise from about 1% to 3% by weight of the composition.

The polyamide-polyamine materials used in this invention are those which have repeating, substituted amido-amine units which correspond to the general Structural Formula No. I as follows:



Structural Formula No. I

In Structural Formula No. I, R_1, R_2 and R_5 are each independently C_{1-4} alkylene, C_{1-4} alkarylene or arylene. It is also possible to eliminate R_1 entirely so that the polyamide-polyamine is derived from oxalic acid.

Also in Structural Formula No. I, R_3 is H, epichlorohydrin, an azetidinium group, an epoxypropyl group or a dimethylaminohydroxypropyl group, and R_4 can be H, C_{1-4} alkyl, C_{1-4} alkaryl, or aryl. R_4 may also be any of the foregoing groups condensed with C_{1-4} alkylene oxide.

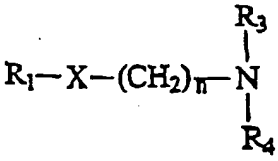
R_1 is preferably butylene, and R_2 and R_5 are preferably ethylene. R_3 is preferably epichlorohydrin. R_4 is preferably H.

The polyamide-polyamine materials useful herein can be prepared by reacting polyamines such as diethylenetriamine, triethylenetetraamine, tetraethylenepentamine or dipropylenetriamine with C_2-C_{12} dicarboxylic acids such as oxalic, succinic, glutaric, adipic and diglycolic acids. Such materials may then be further derivatized by reaction with, for example, epichlorohydrin. Preparation of such materials is described in greater detail in Keim, U.S. Patent 2,296,116, Issued February 23, 1960; Keim, U.S. Patent 2,296,154, Issued February 23, 1960 and Keim, U.S. Patent 3,332,901, Issued July 25, 1967.

The polyamide-polyamine agents preferred for use herein are commercially marketed by Hercules, Inc. under the trade name Kymene®. Especially useful are Kymene 557H® and

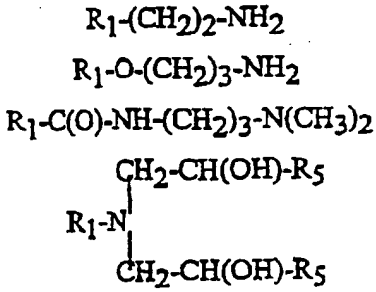
Kymene 557LX® which are epichlorohydrin adducts of polyamide-polyamines which are the reaction products of diethylenetriamine and adipic acid. Other suitable materials are those marketed by Hercules under the trade names Reten® and Delsette®, and by Sandoz under the trade name Cartaretin®. These polyamide-polyamine materials are marketed in the form of aqueous suspensions of the polymeric material containing, for example, about 12.5% by weight of solids.

Detersive Amine - Suitable amine surfactants for use herein include detersive amines according to the formula:



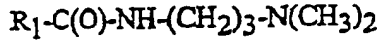
wherein R_1 is a C_6-C_{12} alkyl group; n is from about 2 to about 4, X is a bridging group which is selected from NH, CONH, COO, or O or X can be absent; and R_3 and R_4 are individually selected from H, C_1-C_4 alkyl, or (CH_2-CH_2-O(R_5)) wherein R_5 is H or methyl.

Preferred amines include the following:



wherein R_1 is a C_6-C_{12} alkyl group and R_5 is H or CH_3.

In a highly preferred embodiment, the amine is described by the formula:

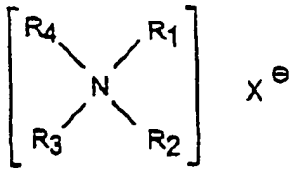


wherein R_1 is C_8-C_{12} alkyl.

Particularly preferred amines include those selected from the group consisting of octyl amine, hexyl amine, decyl amine, dodecyl amine, C_8-C_{12} bis(hydroxyethyl)amine, C_8-C_{12} bis(hydroxyisopropyl)amine, and C_8-C_{12} amido-propyl dimethyl amine, and mixtures.

If utilized the detersive amines comprise from about 0.1% to about 10%, preferably from about 0.5% to about 5%, by weight of the composition.

Quaternary Ammonium Surfactants - from about 1% to about 6% of a quaternary ammonium surfactant having the formula



wherein R_1 and R_2 are individually selected from the group consisting of C_1-C_4 alkyl, C_1-C_4 hydroxy alkyl, benzyl, and $-(C_2H_4O)_xH$ where x has a value from about 2 to about 5; X is an anion; and (1) R_3 and R_4 are each a C_6-C_{14} alkyl or (2) R_3 is a C_6-C_{18} alkyl, and R_4 is selected from the group consisting of C_1-C_{10} alkyl, C_1-C_{10} hydroxy alkyl, benzyl, and $-(C_2H_4O)_xH$ where x has a value from 2 to 5;

Preferred quaternary ammonium surfactants are the chloride, bromide, and methylsulfate salts. Examples of preferred mono-long chain alkyl quaternary ammonium surfactants are those wherein R_1, R_2, and R_4 are each methyl and R_3 is a C_8-C_{16} alkyl; or wherein R_3 is C_{8-18} alkyl and R_1, R_2, and R_4 are selected from methyl and hydroxy-alkyl moieties. Lauryl trimethyl ammonium chloride, myristyl trimethyl ammonium chloride, palmityl trimethyl ammonium chloride, coconut trimethylammonium chloride, coconut trimethylammonium methylsulfate, coconut dimethyl-monohydroxyethyl-ammonium chloride, coconut dimethyl-monohydroxyethylammonium methylsulfate, steryl dimethyl-monohydroxy-ethylammonium chloride, steryl dimethylmonohydroxy-ethylammonium methylsulfate, di- C_{12}-C_{14} alkyl dimethyl ammonium chloride, and mixtures thereof are particularly preferred. ADOGEN 412™, a lauryl trimethyl ammonium chloride commercially available from Witco, is also preferred. Even more highly preferred are the lauryl trimethyl ammonium chloride and myristyl trimethyl ammonium chloride.

Alkoxylated and other quaternary ammonium surfactants which are suitable for use in the present invention are disclosed in detail in the copending patent application of Eugene S. Sadlowski, entitled "Aqueous, Gel, Laundry Detergent Composition", having P&G Case No. 6955, filed under the Patent Cooperation Treaty, Application No. PCT/US98/24809 and international priority date November 26, 1997, which is hereby incorporated by reference.

Polyethoxylated-Polyamine Polymers - Another polymer dispersant form use herein includes polyethoxyated-polyamine polymers (PPP). The preferred polyethoxylated-polyamines useful herein are generally polyalkyleneamines (PAA's), polyalkyleneimines (PAI's), preferably polyethyleneamine (PEA's), polyethyleneimines (PEI's). A common polyalkyleneamine (PAA) is tetrabutylenepentamine. PEA's are obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEA's obtained are

triethylenetetramine (TETA) and teraethylenepentamine (TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See U.S. Patent 2,792,372, Dickinson, issued May 14, 1957, which describes the preparation of PEA's.

Polyethoxylated polyamines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing these polyamine backbones are disclosed in U.S. Patent 2,182,306, Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746, Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095, Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839, Crowther, issued September 17, 1957; and U.S. Patent 2,553,696, Wilson, issued May 21, 1951

Preferred polyethoxyated-polyamine polymers useful for this invention are alkoxylated quaternary diamines and alkoxylated quaternary polyamines which are disclosed in greater detail in the copending patent application of Patrick Delplancke et al., entitled "Aqueous, Gel, Laundry Detergent Composition", having P&G Case No. 6775, filed under the Patent Cooperation Treaty, Application No. PCT/US98/15281 and international priority date July 23, 1998, hereby incorporated by reference.

The levels of these polyethoxyated-polyamine polymers used can range from about 0.1% to about 10%, typically from about 0.4% to about 5%, by weight. These polyethoxyated-polyamine polymers can be synthesized following the methods outline in U.S. Patent No. 4,664,848, or other ways known to those skilled in the art.

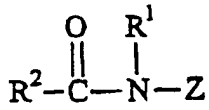
Detersive Surfactants- Surfactants are known to have potentially harsh effects on fabrics. Typically, the compositions herein will comprise from about 3 % to about 40 %, more preferably from about 10 % to about 25 %, most preferably from about 15 % to about 20 %, by weight of detersive surfactants.

Nonlimiting examples of surfactants useful herein include the unsaturated sulfates such as oleyl sulfate, the C_{10}-C_{18} alkyl alkoxy sulfates ("AE_xS"; especially EO 1-7 ethoxy sulfates), C_{10}-C_{18} alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), and primary, branched-chain and random C_{10}-C_{20} alkyl sulfates ("AS"), the C_{10}-C_{18} secondary (2,3) alkyl sulfates of the formula $CH_3(CH_2)_x(CHOSO_3^-M^+)$ CH_3 and CH_3 $(CH_2)_y(CHOSO_3^-M^+)$ CH_2CH_3 where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is

a water-solubilizing cation, especially sodium, the C_{10-18} glycerol ethers, the C_{10}-C_{18} alkyl polyglycosides and their corresponding sulfated polyglycosides, and C_{12}-C_{18} alpha-sulfonated fatty acid esters.

If desired, the conventional nonionic and amphoteric surfactants such as the C_{12}-C_{18} alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C_6-C_{12} alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), C_{12}-C_{18} betaines and sulfobetaines ("sultaines"), C_{10}-C_{18} amine oxides, and the like, can also be included in the overall compositions. The C_{10}-C_{18} N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C_{12}-C_{18} N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C_{10}-C_{18} N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C_{12}-C_{18} glucamides can be used for low sudsing. C_{10}-C_{20} conventional soaps may also be used. If high sudsing is desired, the branched-chain C_{10}-C_{16} soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

Polyhydroxy Fatty Acid Amide Surfactant - The detergent compositions hereof may also contain polyhydroxy fatty acid amide surfactant. The polyhydroxy fatty acid amide surfactant component comprises compounds of the structural formula:



wherein: R^1 is H, C_1-C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferably C_1-C_4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R^2 is a C_5-C_{31} hydrocarbyl, preferably straight chain C_7-C_{19} alkyl or alkenyl, more preferably straight chain C_9-C_{17} alkyl or alkenyl, most preferably straight chain C_{11}-C_{15} alkyl or alkenyl, or mixtures thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z will be a glycityl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of -CH_2-

$(CHOH)_n$-CH_2OH, -$CH(CH_2OH)$-$(CHOH)_{n-1}$-CH_2OH, -CH_2-$(CHOH)_2(CHOR')(CHOH)$-CH_2OH, and alkoxylated derivatives thereof, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide. Most preferred are glycityls wherein n is 4, particularly -CH_2-$(CHOH)_4$-CH_2OH.

R' can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl.

R^2-CO-N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

Z can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymaltotriotityl, etc.

Methods for making polyhydroxy fatty acid amides are known in the art. In general, they can be made by reacting an alkyl amine with a reducing sugar in a reductive amination reaction to form a corresponding N-alkyl polyhydroxyamine, and then reacting the N-alkyl polyhydroxyamine with a fatty aliphatic ester or triglyceride in a condensation/amidation step to form the N-alkyl, N-polyhydroxy fatty acid amide product. Processes for making compositions containing polyhydroxy fatty acid amides are disclosed, for example, in G.B. Patent Specification 809,060, published February 18, 1959, by Thomas Hedley & Co., Ltd., U.S. Patent 2,965,576, issued December 20, 1960 to E. R. Wilson, and U.S. Patent 2,703,798, Anthony M. Schwartz, issued March 8, 1955, and U.S. Patent 1,985,424, issued December 25, 1934 to Piggott, each of which is incorporated herein by reference.

Enzymes - Suitable enzymes include proteases, amylases, lipases, cellulases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active bleach, detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes can be included in the present detergent compositions for a variety of purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains from surfaces such as textiles or dishes, for the prevention of refugee dye transfer, for example in laundering, and for fabric restoration. Enzymes are normally incorporated into detergent or detergent additive compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such

as dishware and the like. In practical terms for current commercial preparations, the compositions herein may comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Suitable detersive enzyme and enzyme stabilizers are further disclosed in greater detail in the copending patent application of Eugene S. Sadlowski, entitled "Aqueous, Gel, Laundry Detergent Composition", having P&G Case No. 6955P, incorporated above.

Enzyme Stabilizing System - Detergent compositions, particularly liquid detergent compositions, that include enzymes should also enzyme stabilizers and chlorine scavengers. The present invention may comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof, and are designed to address different stabilization problems depending on the type and physical form of the detergent composition. See Severson, U.S. 4,537,706 for a review of Borate stabilizers.

Suitable chlorine scavenger anions are widely known and readily available, and, if used, can be salts containing ammonium cations with sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetracetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), and mixtures thereof can likewise be used. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc., and mixtures thereof can be used if desired.

Polymeric Dispersing Agents - Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein, especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptization, and anti-redeposition.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued march 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Other polymeric materials which can be included are polypropylene glycol (PPG), propylene glycol (PG), and polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular

weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

Alkoxylated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula $-(CH_2CH_2O)_m(CH_2)_nCH_3$ wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

The levels of these dispersants used can range from about 0.1% to about 10%, typically from about 0.4% to about 5%, by weight. These dispersants can be synthesized following the methods outline in US. Patent No. 4,664,848, or other ways known to those skilled in the art.

Dye Fixative Materials - optionally but preferred for use herein are selected dye fixative materials which do not form precipitates with anionic surfactant.

The selected dye fixatives useful herein may be in the form of unpolymerized materials, oligomers or polymers. Moreover, the preferred dye fixatives useful herein are cationic. The dye fixative component of the compositions herein will generally comprise from about 0.1% to 5% by the weight of the composition. More preferably, such dye fixative materials will comprise from about 0.5% to 4% by weight of the compositions, most preferably from about 1% to 3%. Such concentrations should be sufficient to provide from about 10 to 100 ppm of the dye fixative in the aqueous washing solutions formed from the laundry detergent compositions herein. More preferably from about 20 to 60 ppm of the dye fixative will be delivered to the aqueous washing solution, most preferably about 50 ppm.

The non-precipitating dye fixatives useful herein include a number that are commercially marketed by CLARIANT Corporation under the Sandofix®, Sandolec® and Polymer VRN® trade names. These include, for example, Sandofix SWE®, Sandofix WA®, Sandolec CT®, Sandolec CS®, Sandolec C1®, Sandolec CF®, Sandolec WA® and Polymer VRN®. Other

suitable dye fixatives are marketed by Ciba-Geigy Corporation under the trade name Cassofix FRN-300® and by Hoechst Celanese Corporation under the trade name Tinofix EW®.

Polymeric Soil Release Agent— Soil release agents may be used in the present invention. If so they will generally comprise from about 0.01 % to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

Any polymeric soil release agent known to those skilled in the art can optionally be employed in the compositions and processes of this invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and its blends, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

The polymeric soil release agents useful herein especially include those soil release agents having: (a) one or more nonionic hydrophile components consisting essentially of (i) polyoxyethylene segments with a degree of polymerization of at least 2, or (ii) oxypropylene or polyoxypropylene segments with a degree of polymerization of from 2 to 10, wherein said hydrophile segment does not encompass any oxypropylene unit unless it is bonded to adjacent moieties at each end by ether linkages, or (iii) a mixture of oxyalkylene units comprising oxyethylene and from 1 to about 30 oxypropylene units wherein said mixture contains a sufficient amount of oxyethylene units such that the hydrophile component has hydrophilicity great enough to increase the hydrophilicity of conventional polyester synthetic fiber surfaces upon deposit of the soil release agent on such surface, said hydrophile segments preferably comprising at least about 25% oxyethylene units and more preferably, especially for such components having about 20 to 30 oxypropylene units, at least about 50% oxyethylene units; or (b) one or more hydrophobe components comprising (i) C_3 oxyalkylene terephthalate segments, wherein, if said hydrophobe components also comprise oxyethylene terephthalate, the ratio of oxyethylene terephthalate:C_3 oxyalkylene terephthalate units is about 2:1 or lower, (ii) C_4-C_6 alkylene or oxy C_4-C_6 alkylene segments, or mixtures therein, (iii) poly (vinyl ester) segments, preferably polyvinyl acetate), having a degree of polymerization of at least 2, or (iv) C_1-C_4 alkyl ether or C_4 hydroxyalkyl ether substituents, or mixtures therein, wherein said substituents are present in the form of C_1-C_4 alkyl ether or C_4 hydroxyalkyl ether cellulose derivatives, or mixtures therein, and such cellulose derivatives are amphiphilic, whereby they have a sufficient level of C_1-C_4

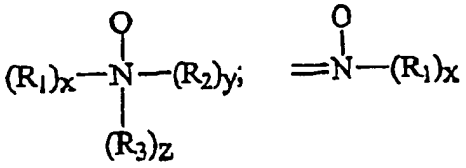
alkyl ether and/or C_4 hydroxyalkyl ether units to deposit upon conventional polyester synthetic fiber surfaces and retain a sufficient level of hydroxyls, once adhered to such conventional synthetic fiber surface, to increase fiber surface hydrophilicity, or a combination of (a) and (b).

Other suitable polymeric soil release agents are disclosed in U.S. Patent No. 5,415,807, issued May 16, 1995 to Gosselink, which is hereby incorporated by reference.

Dye Transfer Inhibiting Agents—The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from about 0.01% to about 10% by weight of the composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%.

More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following structural formula: $R\text{-}A_x\text{-}P$; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: -NC(O)-, -C(O)O-, -S-, -O-, -N=; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:



wherein R_1, R_2, R_3 are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a pKa <10, preferably pKa <7, more preferred pKa <6.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and

mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. Preferred polyamine N-oxide are discussed in greater detail in U.S. Patent No. 5,466,802, issued Nov. 14, 1995 to Panandiker, which is hereby incorporated by reference

Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. Preferred copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers are discussed in greater detail in U.S. Patent No. 5,466,802, incorporated above.

The present invention compositions also may employ a polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

Brightener - Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.01% to about 1.2%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD, the 2-(4-styryl-phenyl)-2H-naptho[1,2-d]triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the amino-coumarins. See also U.S. Patent No. 3,646,015, issued February 29, 1972 to Hamilton and U.S. Patent No. 5,466,802, incorporated above.

Suds Suppressors - Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as described in U.S. 4,489,455 and 4,489,574 and in front-loading European-style washing machines.

A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See U.S. Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

The detergent compositions herein may also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons, N-alkylated amino triazines, monostearyl phosphates, silicone suds suppressors, secondary alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils. Hydrocarbon suds suppressors are described, for example, in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al and European Patent Application No. 89307851.9, published February 7, 1990, by Starch, M. S. Mixtures of alcohols and silicone oils are described in U.S. 4,798,679, 4,075,118 and EP 150,872

Additional examples of all of the aforementioned suds suppressors may be found in the provisional patent application of Pramod K. Reddy, entitled "Hydrophilic Index for Aqueous, Liquid Laundry Detergent Compositions containing LAS", filed under the Patent Cooperation

having P&G Case No. 7332P, filed on November 6, 1998 and having Serial No. 60/107,477, which is hereby incorporated by reference.

Alkoxylated Polycarboxylates - Alkoxylated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq., incorporated herein by reference. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula $-(CH_2CH_2O)_m(CH_2)_nCH_3$ wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

Optional Components—The compositions herein may further contain one or more additional detersive additives selected from the group consisting of polymeric dispersing agents, dyes, colorants, filler salts, through-the-wash fabric softeners, antiredeposition agents, antifading agent, dye fixative agents, prill/fuzzing reducing agents, and mixtures thereof.

Method Aspect

The compositions of this invention can be used to form aqueous washing solutions for use in the laundering of fabrics. Generally, an effective amount of such compositions is added to water, preferably in a conventional fabric laundering automatic washing machine, to form such aqueous laundering solutions. The aqueous washing solution so formed is then contacted, preferably under agitation, with the fabrics to be laundered therewith.

An effective amount of the liquid detergent compositions herein added to water to form aqueous laundering solutions can comprise amounts sufficient to form from about 500 to 7,000 ppm of composition in aqueous solution. More preferably, from about 800 to 3,000 ppm of the detergent compositions herein will be provided in aqueous washing solution.

The following examples are illustrative of the present invention, but are not meant to limit or otherwise define its scope. All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified.

EXAMPLES

Table I

Liquid laundry detergent compositions of the present invention are as follows:

Example	A	B	C	D	E	F
AE2.5S[1]	21	21	20.2	22.7	22.7	13.6
C_{12} LAS	-	-	-	-	-	9.1
C_{12-14} glucosamide	4	4	2.5	-	-	-
AEO7[2]	4.5	4.5	-	-	-	-
AEO9[3]	-	-	0.6	0.6	0.6	0.6
C_{8-10} amidopropylamine	1.3	1.3	-	-	-	-
C_{10} amidopropylamine	-	-	1.3	1.3	1.3	1.3
citric acid	1	3	5	1	2.5	1
C_{12-14} fatty acid	-	-	10	10	8	10
palm kernal fatty acid	8	5.4	-	-	-	-
rapeseed fatty acid	8	5.4	-	-	-	-
protease	0.6	0.6	0.9	0.9	0.9	0.9
lipase	0.07	0.07	0.08	0.08	0.08	0.08
amylase	0.18	0.18	0.15	0.15	0.15	0.15
cellulase	0.03	0.03	0.05	0.05	0.05	0.05
endolase	0.2	0.2	-	-	-	-
brightener	0.15	0.15	0.15	0.15	0.15	0.15
polymer A[4]	0.66	0.66	0.6	0.6	0.6	0.6
polymer B[5]	-	-	1.2	1.2	1.2	1.2
Polyamine-polyamide[6]	2	-	1	1	-	-
Polyethoxylated-Polyamines	-	1	2	-	-	-
soil release agent	-	-	0.1	0.1	0.1	0.1
ethanol	0.7	0.7	0.54	0.54	0.54	0.54
1,2-propanediol	4	4	4	4	4	4
Monoethanolamine	0.7	0.7	0.5	0.5	0.5	0.5
NaOH	2.8	2.8	7	7	7	7
boric acid	2	2	-	-	-	-

borax	-	-	2.5	2.5	2.5	2.5
suds supressor	-	-	0.1	0.1	0.1	0.1
PDMS	0.2	0.2	-	-	-	-
perfume composition[7]	0.5	0.5	0.75	0.75	0.75	0.75
dye	-	-	0.04	0.04	0.04	0.04
water	balance	balance	balance	balance	balance	balance

1: C12-15 alkyl ethoxy sulfonate containing an average of 2.5 ethoxy groups

2: C_{12-14} Alkyl ethoxylated surfactant containing seven ethoxy groups.

3: C_{12-15} Alkyl ethoxylated surfactant containing nine ethoxy groups.

4: Modified polyamines of PEI (MW = 182) with average degree of ethoxylation = 15

5: Modified polyamines of PEI (MW = 600) with average degree of ethoxylation = 20

6: The polyamine-polyamides selected from those compounds marketed under the following trade names: Kymene®, Kymene 557H®, Kymene 557LX®, Reten®, and Cartaretin®.

7: The perfume Composition is selected from the perfume compositions A - I described in table IV (below).

Table II
Liquid laundry detergent compositions of the present invention are as follows:

Example Number	G	H	I	J
AE2.5S[1]	18.12	18.25	22.65	22.65
C_{12} LAS	4.5	-	-	-
AEO9[2]	0.6	5	0.6	0.6
C_{10} amidopropylamine	1.3	1.3	1.3	1.3
citric acid	1	1	1	1
C_{12-14} fatty acid	10	10	10	10
Quaternary Surfactant[3]	0.5	1	5	-
oleic acid	-	-	-	2.5
protease	0.9	0.9	0.9	0.9
lipase	0.08	0.08	0.08	0.08
amylase	0.15	0.15	0.15	0.15
cellulase	0.05	0.05	0.05	0.05
brightener	0.15	0.15	0.15	0.15
polymer A[4]	0.6	0.6	0.3	0.6
polymer B[5]	1.2	1.2	0.6	1.2
soil release agent	0.1	0.1	0.1	0.1
ethanol	0.54	0.54	0.54	0.54
1,2-propanediol	4	4	4	4
Monoethanolamine	0.48	0.48	0.48	0.48
NaOH	7	7	7	7
borax	2.5	2.5	2.5	2.5
suds supressor	0.1	0.1	0.1	0.1
perfume composition[6]	0.75	0.75	0.75	0.75
dye	0.04	0.04	0.04	0.04
water	balance	balance	balance	balance

1: C_{12-15} alkyl ethoxy sulfonate containing an average of 2.5 ethoxy groups

2: C_{12-15} Alkyl ethoxylated surfactant containing nine ethoxy groups.

3: Quaternary Surfactant is selected from one or more of the following: lauryl trimethyl ammonium chloride, myristyl trimethyl ammonium chloride, palmityl trimethyl ammonium chloride, coconut trimethylammonium chloride, coconut trimethylammonium methylsulfate, coconut dimethyl-monohydroxyethyl-ammonium chloride, coconut dimethyl-monohydroxyethylammonium methylsulfate, steryl dimethyl-monohydroxy-ethylammonium chloride, steryl dimethylmonohydroxy-ethylammonium methylsulfate, di- C_{12}-C_{14} alkyl dimethyl ammonium chloride.

4: Modified polyamines of PEI (MW = 182) with average degree of ethoxylation = 15

5: Modified polyamines of PEI (MW = 600) with average degree of ethoxylation = 20

6: The perfume Composition is selected from the perfume compositions A - I described in table IV (below).

Table III
Liquid laundry detergent compositions of the present invention are as follows:

Example Number	K	L	M
AE2.5S[1]	27.65	22.65	22.65
AEO9[2]	0.6	0.6	0.6
C10 amidopropylamine	1.3	1.3	1.3
citric acid	1	1	1
C_{12-14} fatty acid	7.5	5	10
protease	0.9	0.9	0.9
lipase	0.08	0.08	0.08
amylase	0.15	0.15	0.15
cellulase	0.05	0.05	0.05
brightener	0.15	0.15	0.15
polymer A[3]	0.6	0.6	0.6
polymer B[4]	1.2	1.2	1.2
soil release agent	0.1	0.1	0.1
ethanol	0.54	0.54	0.54
1,2-propanediol	4	4	4
Monoethanolamine	0.48	0.48	0.48
NaOH	7	7	7
borax	2.5	-	2.5
suds supressor	0.1	0.1	0.1

perfume composition[5]	0.75	0.75	0.75
dye	0.04	0.04	0.04
water	balance	balance	balance

1: C_{12-15} alkyl ethoxy sulfonate containing an average of 2.5 ethoxy groups

2: C_{12-15} Alkyl ethoxylated surfactant containing nine ethoxy groups.

3: Modified polyamines of PEI (MW = 182) with average degree of ethoxylation = 15

4: Modified polyamines of PEI (MW = 600) with average degree of ethoxylation = 20

5: The perfume Composition is selected from the perfume compositions A - I described in table IV (below).

Fragrance Material Weight %

Table IV

Perfume compositions of the present invention are as follows:

Fragrance Material	A	B	C	D	E	F	G	H	I
dihydromyrcenol	20	0	10	0	10	10	10	18	18
lilial	20	10	10	20	5	10	10	18	18
iso E super	10	10	0	0	0	5	5	9	9
vertenex	10	10	3	0	0	5	5	9	9
ionone Gamma methyl	10	10	10	10	0	5	5	9	9
hexyl cinnamic aldehyde	10	20	10	20	20	5	5	9	9
ionone beta	5	4	0	0	0	2.5	2.5	4.5	4.5
habanolide	5	5	40	10	0	2.5	2.5	4.5	4.5
flor acetate	3	3	3	3	0	1.5	1.5	2.7	2.7
polysantol	3	2	2	3	0	1.5	1.5	2.7	2.7
frutene	2	2	2	0	0	1	1	1.8	1.8
alpha pinene	1	2	0	2	3	0.5	0.5	0.9	0.9
camphene	1	2	0	2	2	0.5	0.5	0.9	0.9
d-limonen	0	20	0	0	40	0	0	0	0
tetrahydro linalool	0	0	10	30	20	0	0	0	0
geraniol	0	0	0	0	0	20	20	5	0
linalool	0	0	0	0	0	10	10	0	0
phenyl ethyl alcohol	0	0	0	0	0	20	15	5	10
hexyl acetate	0	0	0	0	0	0	5	0	0

Eucalyptol	0	0	0	0	0	0	5	0	0
Total	100	100	100	100	100	100	105	100	100

What is claimed is:

1. A heavy duty gel or liquid laundry detergent composition characterized by, by weight of the composition:

a) from 10% to 40% of an anionic surfactant;

b) a perfume composition, wherein at least 1 % of the perfume composition is characterized by fragrance materials selected from the group consisting of fragrance materials having a logP of at least 3; and

c) a structurant.

2. The detergent composition of Claim 1 wherein the detergent composition is transparent.

3. The detergent composition of any of Claims 1-2 wherein the viscosity of the detergent composition is from 100 cps to 4,000 cps when measured at a temperature of 25°C and at a shear rate of 20 s^{-1}.

4. The detergent composition of any of Claims 1-3 wherein the composition is wholly or partly in lamellar form.

5. The detergent composition of any of Claims 1-4 wherein the structurant is characterized by an electrolyte and a detergent builder, and the ratio of electrolyte to detergent builder is from 10:1 to 1:10.

6. The detergent composition of any of Claims 1-5 wherein the perfume composition further is characterized by from 1% to 90% of a fragrance material having a boiling point of at least 250° C.

7. A heavy duty liquid or gel laundry detergent composition which is either wholly or partly in lamellar form and is characterized by, by weight of the composition:

a) from 10% to 40% of an anionic surfactant;

b) from 0.1% to 3.0% of a perfume composition, wherein at least 1.0% of the perfume composition is characterized by fragrance materials selected from the group consisting of fragrance materials having a logP of at least 3;

c) at least 0.5% of a structurant; and

d) an amine selected from the group consisting of detersive amines, modified polyamines, polyamide-polyamines, polyethoxylated-polyamine polymers, quaternary ammonium surfactants, and mixtures thereof;

wherein the viscosity of the detergent composition is from 100 cps to 4,000 cps when measured at a temperature of 25°C and at a shear rate of 20 s^{-1}.

8. The detergent composition of any of Claims 1-7 wherein the perfume composition further comprises from 1% to 90% of a fragrance material having a boiling point of at least 250° C.

9. The detergent composition of any of Claims 1-8 wherein the structurant comprises an electrolyte and a detergent builder, and the ratio of electrolyte to detergent builder is from 10:1 to 1:10.

10. A detergent composition substantially as described herein with reference to the examples.

11. A method of cleaning a textile fabric characterised by the steps of:

(i) preparing a liquid or gel laundry detergent composition according to any of claims 1 to 10

(ii) dissolving an effective amount of the detergent composition in water to form an aqueous solution; and

(iii) contacting the textile fabric with the aqueous solution.